Dielectric Relaxation and Mechanical Investigation of Ethylene Propylene Diene Monomer Rubber with Some Crosslinking Additives

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ABSTRACT: A systematic dielectric study over a frequency range from 100 Hz to 10 MHz was carried out on ethylene propylene diene monomer rubber (EPDM) mixed with zinc chloride and ammonium iodide with increasing quantities up to 16 and 8 phr, respectively. The measurements were carried out at a room temperature of ≈ 25°C. Dielectric data were fitted in the frequency domain by using three Fröhlich terms discussing the different relaxation mechanisms in the system. These terms were interpreted according to the crosslinking that is formed by the addition of such materials to EPDM. The thermal aging for such systems was also studied and the data obtained are compared with those done before aging. The mechanical properties as well as the thermal gravimetric measurements were also studied and the data obtained are discussed.
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Key words: dielectric relaxation; mechanical investigation; rubber; crosslinking additives

INTRODUCTION

The use of coagents in conjunction with peroxides to cure elastomers was a common practice in the rubber industry[1] for many years. Coagents are typically multifunctional monomers that are highly reactive in the presence of free radicals and readily graft to elastomer chains to form a complex crosslink network. With peroxide-cured elastomers, they not only increase the crosslinking efficiency of the vulcanization process, but also increase the crosslink density as well. The increase in the crosslinking density is directly related to the coagent concentration and has a major impact on the mechanical and physical properties of the cured elastomer. Zinc salts as crosslinkers of acrylic acid and methacrylic acid proved to be the most effective of the metal salts and are used extensively in the manufacture of golf ball cores today.[1]

Presently, the interest is led by the growing importance of microwave processing of materials.[2] This requires a detailed knowledge of the dielectric properties of the crosslink process. The dielectric relaxation spectrum of polymers is very broad and the relaxation processes occur on a very large time scale; thus, for a complete characterization, some decades of frequencies should be analyzed, which is hard to achieve.[3] However, not withstanding the improvements of the experimental techniques, a thorough understanding of the relationships between dielec-

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Table I Rheometric Characteristics and Physico–Mechanical Properties of EPDM Vulcanizates Containing Zinc Chloride

	Sample No.				
	N_1	N_2	N_3	N_4	N_5
Zinc chloride phr	—	4	8	12	16
Rheometric Characteristics at 152 ± 1°C					
M_L, dN m	17.00	14.00	13.50	9.00	8.50
M_H, dN m	84.50	45.00	35.50	31.00	29.50
t_{s2}, min	3.10	2.50	3.00	4.00	3.50
t_{C90}, min	46.50	33.00	27.50	37.50	31.00
CRI, min^{-1}	2.30	3.30	4.10	3.50	3.60
Mechanical Properties					
M-100, MPa	1.13	1.07	0.96	0.87	0.84
T.S., MPa	2.19	4.96	6.32	4.85	1.80
Elongation, %	193.00	588.00	650.00	439.00	177.00
Swelling in toluene	180.00	201.00	220.00	205.00	190.00
Soluble fraction, %	3.50	4.00	3.50	3.40	3.20

Base recipe: EPDM: 100, Dicumyl Peroxide 4.0. M_L, minimum torque; M_H, maximum torque; t_{s2}, scorch time at 2 torque units after minimum; t_{C90}, optimum cure time (at 90% cure); CRI, cure rate index [CRI = $1/(t_{c90} - t_{s2})$]; M-100, modulus at 100% strain; T.S., tensile strength.

tric and molecular parameters is still to be gained.

The present work shows zinc chloride and ammonium iodide used as coagents for curing ethylene propylene diene monomer rubber (EPDM). It is also aimed at using the dielectric method to follow the change in relaxation mechanisms in the presence of such coagents. In addition, it studies the mechanical properties as well as the gravimetric properties. The effect of thermal aging on the electrical and mechanical properties is also considered.

EXPERIMENTAL

Materials

Rubber

EPDM : Ethylene norbornene with ethylene [weight content, 70%; unsaturated ratio, DB/100c 8 and 22% propylene; M_L (1 + 4) (money viscosity) 85] and EPDM 447 were obtained from the BUNA Ap.

Filler. Semireinforcing furnace black (SRF); specific gravity (sp. gr.) 1.78–1.82; pH, 8.5–10) was used as filler.

Accelerators. Tetramethylthiuram disulphide (TMTD; sp. gr. 1.4–1.44; melting point, 143.3°C; physical form, white powder or pellets; fineness, 99.9% through 100 mesh) and Mercaptobenzothiazol (MBT; sp. gr., 1.49; melting point, 177°C; physical form pale yellow powder; fineness, 99.8% through 100 mesh) were used as accelerators.

Rubber Ingredients. Dicumyl peroxide, stearic acid, zinc oxide, SRF, processing oil, MBT, TMTD, and sulfur were used in pure grade.

Solvents and Chemicals. Toluene as a solvent, and zinc chloride and ammonium iodide as coagents were used in pure grade.

Techniques

Melt Mixing. The rubber and the coagent zinc chloride or ammonium iodide were mixed in a Barabender plasticorder at 150°C and a rotor speed of 30 rpm. The mixing was continued for 5 min and then peroxide or the other ingredients were added to the mix on a laboratory two-roll mill (470-mm diameter; 300-mm working distance; 24 rev/min, speed of the slow roll; 1 : 1.4, gear ratio). The compounded rubber was left overnight before vulcanization.

Vulcanization. The vulcanization was carried out in a heated platen press under pressure of about 40 kg/cm^2 and a temperature of 152 ± 1°C.

Table II Rheometric Characteristics and Physico–Mechanical Properties of EPDM Vulcanizates Containing Ammonium Iodide

	Sample No.					
	N_1	D_1	D_2	D_3	D_4	D_5
Ammonium Iodide, phr	—	1	2	3	4	5
Rheometric Characteristics at 152 ± 1°C						
M_L, dN m	17.0	15.0	16.0	16.5	16.5	17.8
M_H, dN m	84.5	87.0	88.0	83.5	84.0	85.0
t_{s2}, min	3.1	2.8	2.5	2.8	2.3	2.8
t_{C90}, min	46.5	35.5	35.5	35.5	35.0	32.5
CRI, min^{-1}	2.3	—	—	—	—	—
Mechanical Properties						
M-100, MPa	1.13	1.11	1.26	1.22	1.20	1.19
T.S., MPa	2.19	3.45	3.56	3.61	3.22	3.09
Elongation, %	193	425	440	425	275	250
Swelling in toluene	180	264	183	352	174	200
Soluble fraction, %	3.5	4.0	3.5	3.4	3.2	—

Base recipe: EPDM: 100, Dicumyl Peroxide 4.0.

Test of Rubber Mixes and Vulcanizates. ASTM D2084-76T (1972) for determination rheometric characteristic of M_L, M_H, t_{s2}, t_{c90}, and CRI using a Monsanto Rheometer 100, ASTM D 412-66T (1967) for determination of physicomechanical properties using a Zwick tensile testing machine (model 1425), and ASTM D573 (1952) for thermal aging equilibrium swelling in toluene[4] were compared. Thermal degradation was studied using a Shimadzu Analyzer TGA (50°C) in a temperature range from 25 to 800°C at a heating rate 10°C/min.

Dielectric Measurements. The permittivity ε' and dielectric loss ε'' in the frequency range 100 Hz up to 10 MHz were measured using the following instruments. (1) An LCR meter-type AG-411 B (Ando Electric Ltd., Japan) in the frequency range between 100 Hz and 100 kHz was used. The capacitance C and the loss tangent tan δ were measured directly from the bridge from which ε' and ε'' were calculated. (2) At a frequency range from 100 kHz to 10 MHz, a circuit magnification meter Q, meter-type TF 1246 (Marconi Instruments, England) was used to measure the capacitance C and the loss tangent tan δ from which ε' and ε'' were calculated. (3) A guard ring capacitor-type NFM/5T [Wiss Tech. Werkstatten (WTW) GMBH, Germany] was used as a measuring cell. The cell was calibrated by using standard materials (trolitul, glass, and air) with different thicknesses ranging from 1 to 4 mm. For each sample, a relation between the thickness d and its capacitance C_M was plotted as a standard curve. The capacitance C_M for the standard materials obtained from the standard curves is plotted versus the known permittivity ε' of each material ($\varepsilon' = 1$, 2.54, and 7 for air, trolitul, and glass, respectively). The relation between C_M and ε' was found to be linear, and thus, the permittivity corresponding to any measured capacitance can then be deduced. To check the standard curves, two teflon samples ($\varepsilon' = 2.0$)[5] with different thicknesses were used. The experimental error in ε' and ε'' in both instruments are found to be ± 3 and $\pm 5\%$, respectively.

Electrical Conductivity Measurements. To measure the dc conductivity σ of the samples, a power supply unit OM 451/01 (Philips) was used to give a stable dc voltage between 0 and 250 V with a maximum permissible loading current of 1 mA. The potential difference (V) between the plates holding the sample and the current (I) flowing through it was measured by multimeter-type URI/BN 1050 (Rhode and Schwarz, Germany). The cell used for the electrical conductivity measurements was that used in the case of dielectric measurements.

RESULTS AND DISCUSSION

Zinc difunctional salts were used as crosslinking coagents for peroxide-curing EPDM. It was be-

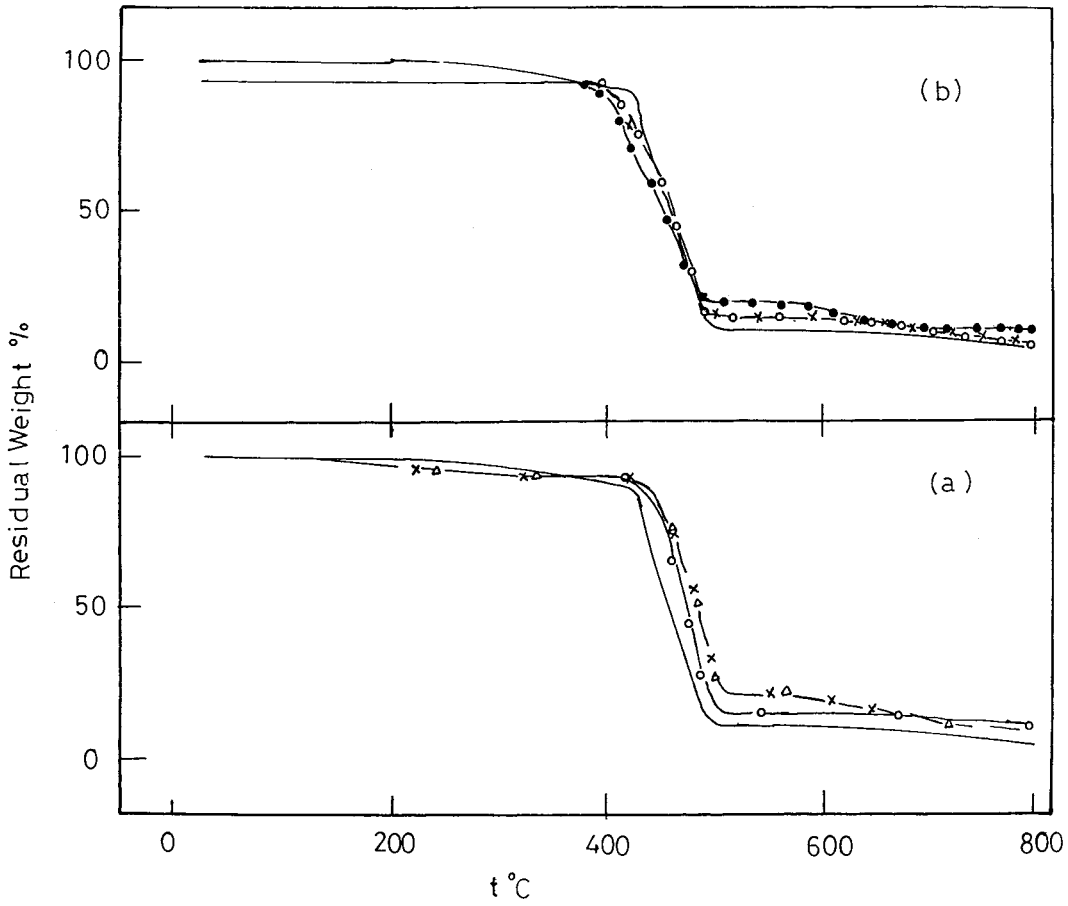

Figure 1 Thermal gravimetric curves for EPDM with (a) (——) N_1, (○) N_2, (×) N_3, and (△) N_5; (b) (——) N_1, (●) D_1, (○) D_3, and (×) D_5. Same notations as in Tables I and II.

lieved that an ionic crosslinking mechanism occurred to increase the tensile properties of the vulcanizates.[1] For this purpose, zinc chloride was chosen to study its effect on the crosslinking and on the thermal stability of EPDM cured by peroxide. Ammonium iodide was also examined as a thermal stabilizer because of the presence of halogens, which can act as fire retardants.

Table I shows EPDM formulations containing different amounts of zinc chloride up to 16 phr. The rheometric characteristics were also determined and listed in the same table. It is clear that zinc chloride decreases both the scorch time and the optimum cure time up to 8 phr.

The physicomechanical properties were determined for the vulcanizates and given in Table I. It is shown that zinc chloride improves the mechanical properties (i.e., increases both tensile strength and elongation at break). This can explained by the ionic crosslinking action of zinc salts, which increases the degree of crosslinking of the prepared vulcanizates.

Ammonium iodide was added to EPDM mixes in different amounts from 1 to 5 phr as shown in Table II, which includes also the rheometric characteristics as well as the physicomechanical properties of the vulcanizates. From this data, it is seen that ammonium iodide has a slight effect on the properties of EPDM vulcanizates.

For the thermal gravimetric TG curve of EPDM, Figure 1 shows that the first loss in weight occurs at 291–427.3°C. This loss, which is about 10% of the total sample, may be attributed to the volatilization of organic compounds of relative small molecular weight that may be present from the manufacturing process of EPDM. Another loss occurs from 427.3 to 430°C, which is considered to be a very small temperature range. This loss corresponds to another 10% of the weight of the sample. This very small loss may be

Table III Rheometric Characteristics and Physico–Mechanical Properties before and after Aging for EPDM Vulcanizates Containing Zinc Chloride

	Sample No.				
	A_1	A_2	A_3	A_4	A_5
Zinc chloride, phr	—	4	8	12	16
Rheometric Characteristics at 152 ± 1°C					
M_L, dN m	13.5	7.5	8.	9.0	8.3
M_H, dN m	67.0	52.5	40.0	35.0	31.0
t_{s2}, min	3.0	2.3	2.3	2.5	2.0
t_{C90}, min	26.5	23.0	29.5	31.0	33.0
CRI, min^{-1}	4.3	4.9	3.7	3.5	3.2
Mechanical Properties before Aging					
M-100, MPa	2.06	1.90	1.75	1.50	1.48
T.S., MPa	13.7	20.0	20.4	17.6	11.3
Elongation, %	425	612	660	602	550
Swelling in toluene	116.3	127	140	128	219
Mechanical Properties after Aging (7 Days at 90°C)					
M-100, MPa	2.35	2.03	2.07	1.91	3.74
T.S., MPa	9.45	9.60	10.20	12.10	13.80
Elongation, %	272	336	435	454	352

Base recipe: EPDM 100, Stearic acid 1.5, Zinc oxide 5, SRF 35, Processing oil 3, MBT 0.8, TMTD 0.8, Sulfur 1.5.

attributed to the thermal degradation of the unvulcanized EPDM part. Up to 600°C, there is a gradual loss in weight (61.5% of the sample's weight). This lower rate is attributed to the breakdown of stronger bonds formed by vulcanization, which combines both breakdown of long chains and bonds to fragments that easily vaporize to the gaseous phase. From 600 to 800°C, there is a very small loss in weight, which corresponds to the removal of residue and ash formation.

Table IV Rheometric Characteristics and Physico–Mechanical Properties before and after Aging for EPDM Vulcanizates Containing Ammonium Iodide

	Sample No.						
	A_1	B_1	B_2	B_3	B_4	B_5	B_6
Ammonium iodide, phr	—	12	3	4	5	8	
Rheometric Characteristics at 152 ± 1°C							
M_L, dN m	13.5	12.0	6.0	5.0	5.0	6.5	5.0
M_H, dN m	67.0	71.5	53.0	41.0	34.0	30.0	26.0
t_{s2}, min	3.0	2.1	2.0	2.4	2.5	2.0	2.0
t_{C90}, min	26.5	29.5	21.0	20.0	27.5	29.0	30.0
CRI, min^{-1}	4.3	3.7	5.3	5.7	4.0	3.7	3.6
Mechanical Properties before Aging							
M-100, MPa	2.06	2.48	2.557	2.74	2.62	2.25	2.60
T.S., MPa	13.7	11.50	11.23	13.67	13.59	14.89	12.81
Elongation, %	425	366	324	330	327	420	336
Swelling in Toluene	116.3	151	136	135	134	149	134
Mechanical Properties after Aging (7 Days at 90°C)							
M-100, MPa	2.35	3.83	3.40	3.72	3.85	2.99	3.88
T.S., MPa	9.45	8.40	9.30	9.14	8.42	8.60	7.10
Elongation, %	272	204	223	226	198	219	181

Base recipe: EPDM 100, Stearic acid 1.5, Zinc oxide 5, SRF 35, Processing oil 3, MBT 0.8, TMTD 0.8, Sulfur 1.5.

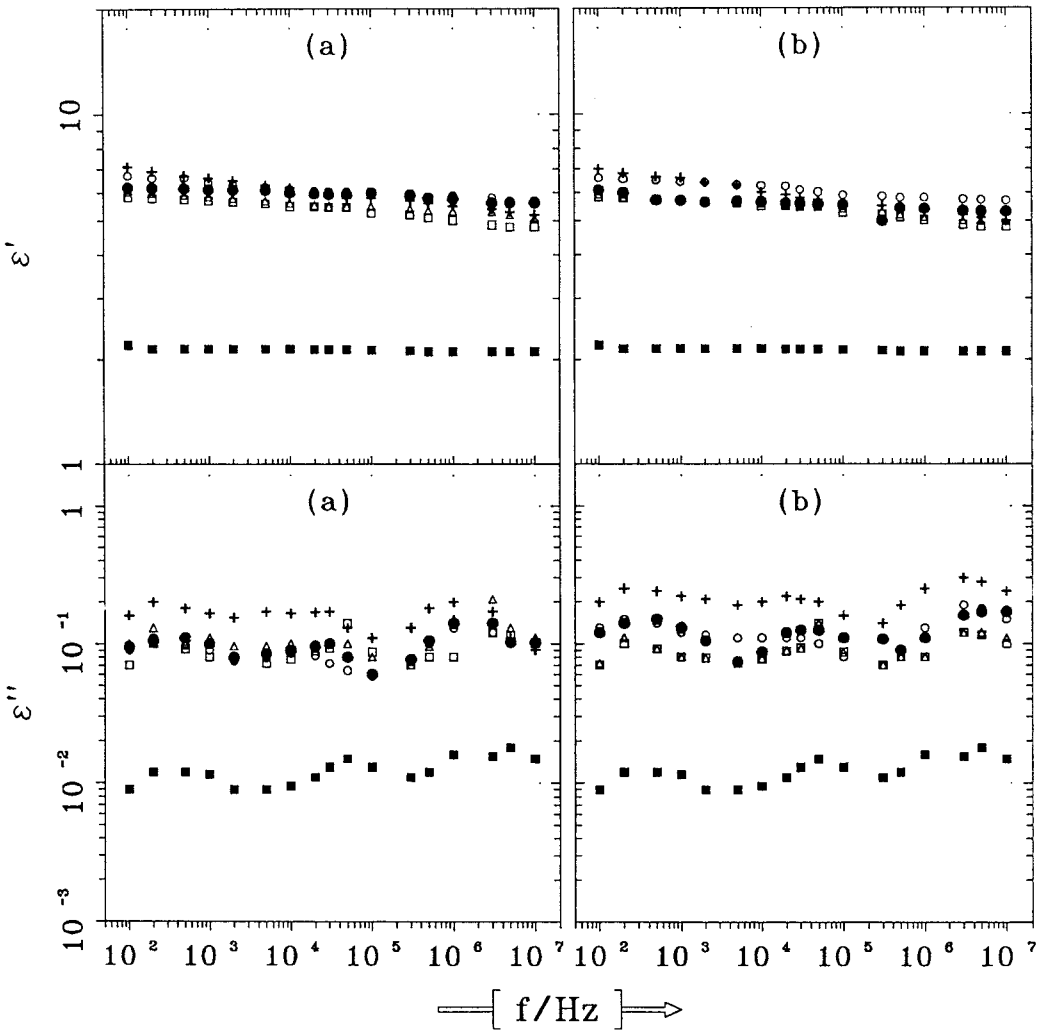

Figure 2 The permittivity ε' and dielectric loss ε'' for (■) N_1, (□) A_1, (△) A_2, (●) A_3, (○) A_4, and (+) A_5; (a) before aging, (b) after 7 days aging at 90°C. Same notations as in Tables I and III.

Adding zinc chloride raises the onset temperature of degradation. These temperatures were 430, 436.4, and 436.4°C for 4, 8, and 12 phr, respectively. Any further addition had no effect on the thermal behavior of EPDM. This rise in temperature (shown in the TG curves as a shift to higher temperatures) may be attributed to the formation of crosslinks that increase with the increase of zinc chloride to some extent (i.e., 12 phr), after which no more crosslinking is promoted.

The addition of ammonium iodide did not show the same trend as the temperature dropped to 400°C and then rose to 410°C for 1 and 3 phr, respectively. The addition of more ammonium iodide had no effect on thermal behavior. This may explained by the formation of a compound between ammonium iodide and EPDM. This compound is less stable than EPDM, so it begins degrading at a lower temperature. With the consequent addition of ammonium iodide, more links are formed, thus avoiding the effect of the formed compound, and consequently, the value of the onset temperature becomes higher.

It is clear from the obtained results that the addition of zinc chloride to EPDM cured with peroxide highly improves the mechanical properties with slight effect on its thermal stability, whereas ammonium iodide has little effect. Thus, it is interesting to study the effect of both zinc chloride and ammonium iodide as vulcanizing coagents with conventional sulfur vulcanizing sys-

Table V Relaxation Parameters of Zinc Chloride

	Sample No.					
	N_1	A_1	A_2	A_3	A_4	A_5
			Before Aging			
P_1	2.8	2.8	2.8	2.8	2.8	2.8
$\varepsilon_1''^*$	0.30	0.32	0.30	0.32	0.33	0.33
$\tau_1 \times 10^{+4}$ s	4.0	4.2	5.3	5.3	5.3	5.3
P_2	2.8	2.8	2.8	2.0	2.0	2.0
$\varepsilon_2''^*$	0.32	0.32	0.25	0.25	0.24	0.25
$\tau_2 \times 10^{+6}$ s	3.2	4.0	8.0	10.6	10.6	10.6
P_3	2.8	2.8	1.6	1.6	1.6	1.6
$\varepsilon_3''^*$	0.38	0.37	0.45	0.43	0.43	0.42
$\tau_3 \times 10^{+8}$ s	2.9	3.2	5.3	10.6	10.6	10.6
			After Aging (7 Days at 90°C)			
P_1	2.8	2.8	2.8	2.8	2.8	2.8
$\varepsilon_1''^*$	0.30	0.32	0.32	0.34	0.34	0.34
$\tau_1 \times 10^{+4}$ s	4.0	4.2	4.2	4.2	4.2	4.2
P_2	2.8	2.8	2.8	2.8	2.8	2.8
$\varepsilon_2''^*$	0.32	0.32	0.32	0.27	0.24	0.25
$\tau_2 \times 10^{+6}$ s	3.2	4.0	4.0	4.0	7.7	8.0
P_3	2.8	2.8	2.8	2.8	2.0	2.0
$\varepsilon_3''^*$	0.38	0.37	0.37	0.39	0.42	0.41
$\tau_3 \times 10^{+8}$ s	2.9	3.2	3.2	3.2	4.6	5.3

P is the distribution parameter, $\varepsilon''^* = \varepsilon''_{max}/\Sigma\ \varepsilon''$, where ε''_{max} is the value of dielectric loss at maximum for each process and τ is the relaxation time in second.

tems. For this purpose, complete mixes were prepared as shown in Tables III and IV.

Table III shows the formulations containing different amounts of zinc chloride up to 16 phr, as well as their rheometric characteristics and the physicomechanical properties of the obtained vulcanizates. From the obtained data, it is clear that the initial addition of zinc chloride decreases the optimum cure time, which is increased with further increase of zinc chloride, whereas the tensile strength and the elongation at break were increased to a maximum value for the samples containing 8 phr zinc chloride. Then, a slight decrease occurred with a further increase of the concentration of zinc chloride.

The prepared samples were subjected to thermal oxidative aging at 90°C for 7 days and the mechanical properties were determined after aging and listed in Table III. It is shown that all the samples suffer from degradation after aging, especially the samples containing lower amounts of zinc chloride, whereas those containing higher amounts (12 and 16 phr) possess higher values of their mechanical properties that can be explained by the remaining partial crosslinking.

Table IV contains the EPDM formulations with different amounts of ammonium iodide up to 8 phr, and their rheometric characteristics as well as the physicomechanical properties of the vulcanizates.

From the obtained results, it is clear that the increase of ammonium iodide content decreases both the maximum and minimum torque and reduces the optimum cure time up to 3 phr. It then increases with the addition of more ammonium iodide. On the other hand, the addition of ammonium iodide has no remarkable effect on the tensile strength, whereas it highly decreases the elongation at break. The mechanical properties were determined after aging at 90°C for 7 days and are listed in Table IV. It is clear that the addition of ammonium iodide has no remarkable effect on the mechanical properties after aging.

The permittivity ε' and the dielectric loss ε'' of the unloaded EPDM rubber sample and that containing the full ingredients in addition to 35 phr SRF carbon black were measured at room temperature ($\approx$ 25°C) and at different frequencies ranging from 100 Hz to 10 MHz. The obtained data are illustrated graphically in Figure 2.

From this figure, it is clear that the values of ε' decrease by increasing the applied frequency, showing an anomalous dispersion. Such dispersion is caused by the dielectric relaxation in

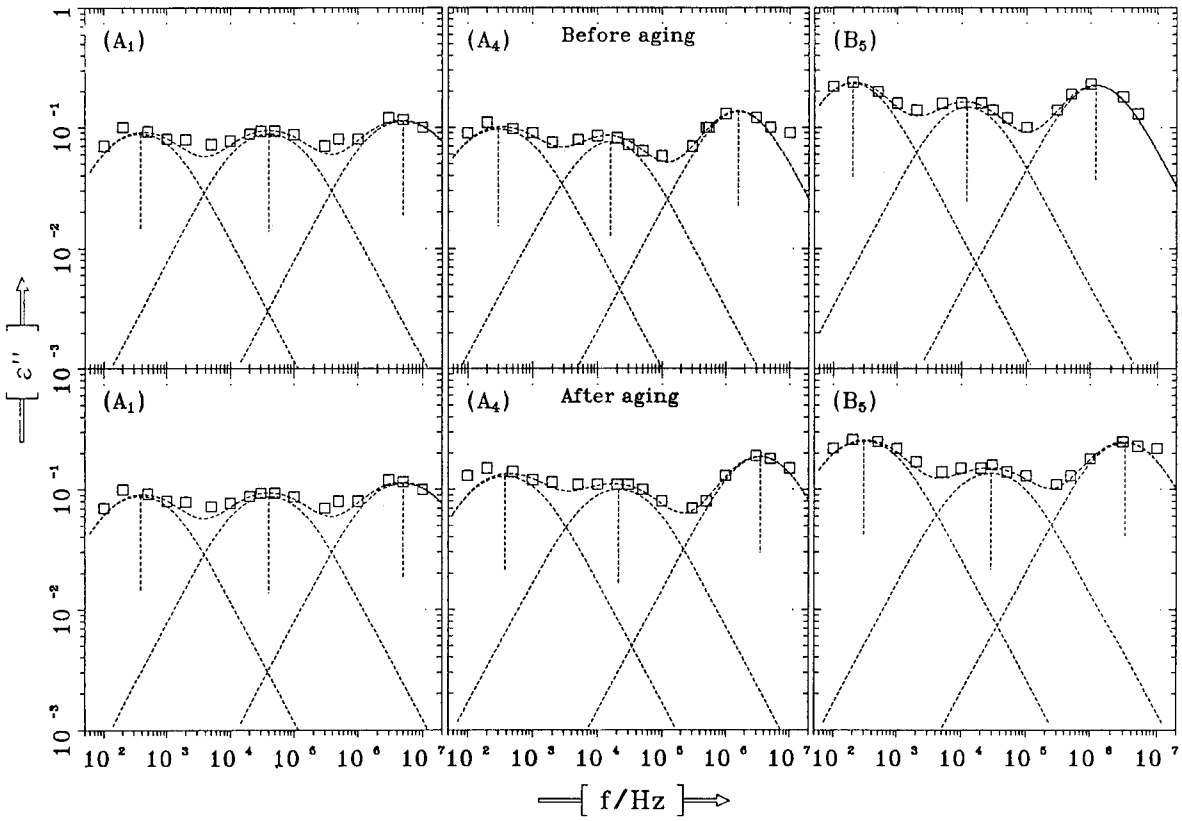

Figure 3 The absorption curves of Samples A_1, A_4, and B_5 before and after 7 days aging. Fitting the experimental ε'' values (□) using three Fröhlich terms. Same notations as in Tables III and IV.

which the permittivity decreases by increasing frequency. Also, it is clear that the values of ε' increase by the addition of 35 SRF black. This is an expected result, as the carbon black provides interfaces and charge carriers and could be the cause of the increase in permittivities.[6] The values of ε' are comparable with those found in the literature.[7]

The variation of ε'' with the applied frequency given in Figure 2 indicates that more than one relaxation process is present. The data were satisfactorily described by a combination of three Fröhlich terms according to the Fröhlich equation.[8] The fitted parameters, relaxation times τ_i and $\varepsilon^{*\prime\prime}$, which is equal to $\varepsilon''_m/\Sigma\ \varepsilon''_m$ and considered to be a measure for the contribution of each process with respect to the other processes, were obtained and given in Table V. An example of the analyses for the EPDM sample loaded with 35 SRF is illustrated graphically in Figure 3. From this figure, it is interesting to find that the three absorption regions are accurately defined as they lie within the available range of frequency and found to be comparable with those found before.[8]

The low-frequency region reaches maximum absorption at about 400 Hz due to dc conductivity or Maxwell–Wagner effect. The dc conductivity for the samples were measured by applying Ohm's law dc flow through the sample at voltage between 0 and 150. No dc was detected, indicating that there is no dc conductivity. It was ascertained that this effect is not due to bad contact between the sample and the condenser plates, as the measurements were repeated with aluminum foil stuck to the two faces of the samples and no change in the results were noticed. In any case, this region is considered to be a Maxwell–Wagner effect (ε''_{MW}), which is due to an ac current that is in phase with the applied potential. This current results from a difference of the conductivities and permittivities of the substances composing the vulcanized EPDM rubber samples. This region is pronouncedly noticed for different types of rubber with different additives.[6–9] The second relaxation mechanism, which lies at a frequency of 50 kHz and found to be slightly higher when the full ingredients (in addition to 35 phr SRF) were added to rubber, could be attributed to the orien-

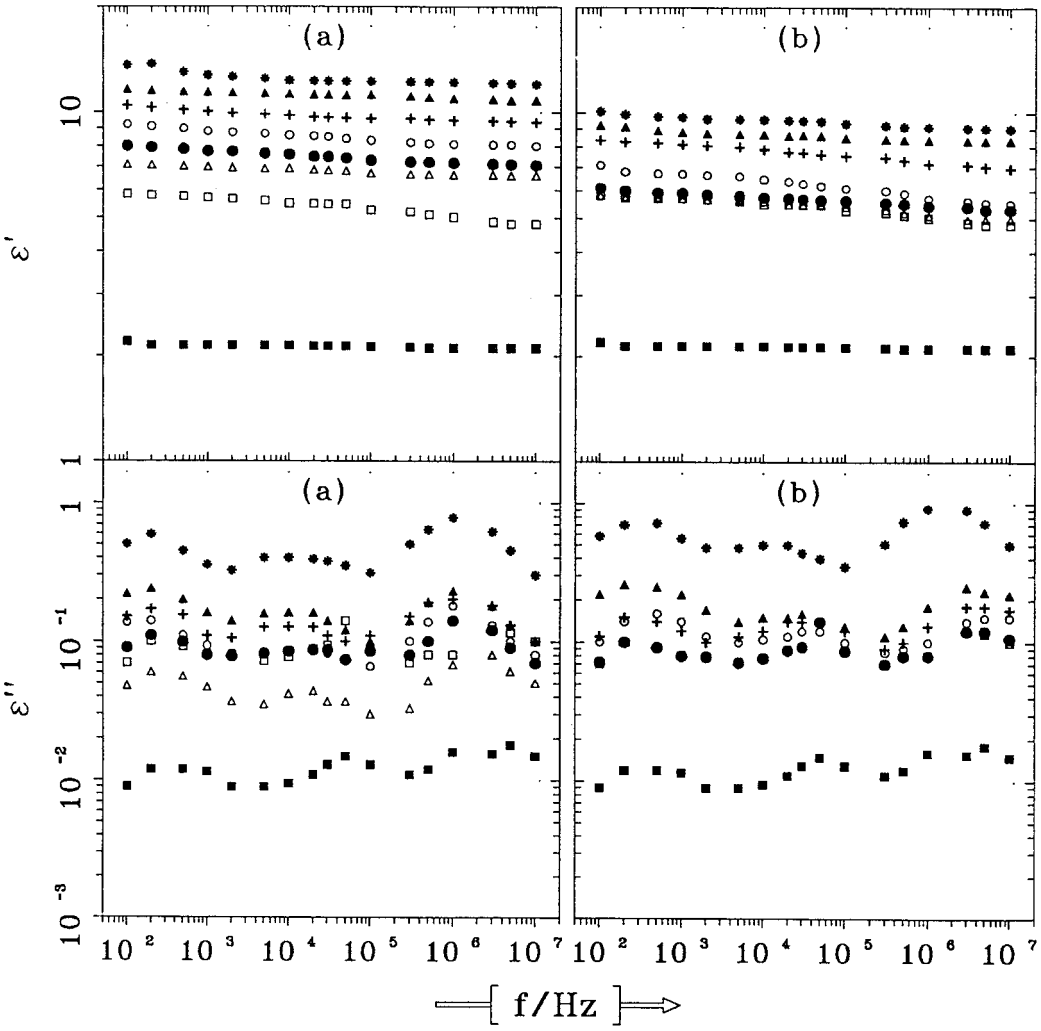

Figure 4 The permittivity ε' and dielectric loss ε'' for (■) N_1, (□) A_1, (△) B_1, (●) B_2, (○) B_3, (+) B_4, (△) B_5, and (*) B_6; (a) before aging, (b) after 7 days aging at 90°C. Same notations as in Tables I, III, and IV.

tation of the large aggregates caused by movement of the main chain that are expected to be formed by the addition of ingredients to rubber. The third relaxation time, which lies on the order of 10^{-8} s, should be associated with those orientations of small aggregates caused by the movement of the main chain (rotation caused by movement of the main backbone). Both regions are found to be in fair agreement with that detected in the literature.[7–9]

The aim of the present investigation is to study the effect of the addition of zinc chloride and ammonium iodide as crosslinking coagents in conjunction with the full ingredients to cure EPDM. For such purposes, different ratios from zinc chloride (4–16 phr) and ammonium iodide (1–8 phr) were added to the same investigated sample that contained 35 phr SRF black. The same measurements were carried out on the prepared samples and the data of ε' and ε'' obtained at the different frequencies are illustrated graphically in Figures 2 and 4. From these two figures, it is clear that ε' and ε'' increases by increasing the content of either zinc chloride or ammonium iodide. This increase is much more pronounced in the case of ammonium iodide, despite the fact that its concentration is less than that of zinc chloride.

The absorption curves relating ε'' and the applied frequency were analyzed into three Fröhlich terms[8] and the obtained data are listed in Tables V and VI. From both tables, it is clear that the values of the first absorption region τ_1, which was

Table VI Relaxation Parameters of Ammonium Iodide

	Sample No.							
	N1	A1	B1	B2	B3	B4	B5	B6
				Before Aging				
P_1	2.8	2.8	2.0	2.0	2.0	2.0	2.0	2.0
$\varepsilon_1''^*$	0.30	0.32	0.32	0.32	0.33	0.33	0.34	0.32
$\tau_1 \times 10^{+4}$ s	4.0	4.2	5.3	5.30	8.0	8.0	8.0	8.0
P_2	2.8	2.8	2.0	2.0	2.0	2.0	2.0	2.0
$\varepsilon_2''^*$	0.32	0.32	0.24	0.25	0.22	0.25	0.25	0.23
$\tau_2 \times 10^{+6}$ s	3.2	4.0	9.4	10.30	13.3	13.3	13.3	13.3
P_3	2.8	2.8	2.0	1.60	1.6	1.6	1.6	1.6
$\varepsilon_3''^*$	0.38	0.37	0.44	0.43	0.45	0.42	0.41	0.45
$\tau_3 \times 10^{+8}$ s	2.9	3.2	8.0	10.60	13.3	13.3	13.3	13.3
				After Aging (7 Days at 90°C)				
P_1	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
$\varepsilon_1''^*$	0.30	0.32	0.32	0.32	0.36	0.32	0.30	0.33
$\tau_1 \times 10^{+4}$ s	4.0	4.2	4.2	4.2	4.2	4.7	4.9	5.3
P_2	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.0
$\varepsilon_2''^*$	0.23	0.32	0.32	0.32	0.29	0.30	0.26	0.23
$\tau_2 \times 10^{+6}$ s	3.2	4.0	4.0	4.0	4.4	5.0	5.5	8.0
P_3	2.8	2.8	2.8	2.8	2.8	2.0	2.0	2.0
$\varepsilon_3''^*$	0.38	0.37	0.37	0.37	0.36	0.38	0.44	0.44
$\tau_3 \times 10^{+8}$ s	2.9	3.2	3.2	3.2	3.5	4.0	5.0	10.0

P is the distribution parameter, $\varepsilon''^* = \varepsilon''_{max}/\Sigma\ \varepsilon''$, where ε''_{max} is the value of dielectric loss at maximum for each process and τ is the relaxation time in second.

associated with the Maxwell–Wagner effect, is slightly affected by the increase in the content of either zinc chloride or ammonium iodide, except for the higher concentration of ammonium iodide (3–8 phr). This increase may be due to the fact that the crosslinking reaction not only changes the molecular mobilities but also some redistribution of the structure. As discussed before,[10] the changes in the defect concentration is connected with changes in free volume, and consequently, with changes in the Maxwell–Wagner interfacial polarization. Also, it is noticed that for both added coagents, the contribution of this absorption region with respect to the other absorption regions $\varepsilon_1''^*$ remains almost unchanged.

The second absorption region, which is ascribed to the large aggregates expected to be formed by the addition of different ingredients to rubber, is found to increase by the addition of both coagents up to a certain concentration beyond which a stability in τ_2 was noticed. This increase is found to be much faster in the case of ammonium iodide, as the value of $\tau_2 = 9.4 \times 10^{-6}$ s after the addition of 1 phr of ammonium iodide, whereas, it is 8×10^{-6} s for the sample containing 4% zinc chloride. The increase in τ_2, which is followed by a decrease in its contribution with respect to the other regions, indicates that large aggregates are expected to be formed by the addition of zinc chloride and ammonium iodide as a result of the formation of partial crosslinking between these coagents and EPDM. This crosslinking may increase by increasing the percentage of the added coagents until a certain concentration, beyond which some sort of stability may occur (i.e., τ_2 is almost unchanged).

The third relaxation process, which could be caused by the Debye losses associated with the movements of the main backbone, is also found to increase by increasing either zinc chloride or ammonium iodide until a certain concentration beyond which the values of τ_3 becomes stable. Moreover, an increase in the values of $\varepsilon_3''^*$ is noticed by the formation of such crosslinking. This is an expected result, as the presence of the crosslinking increases the size of the main chain, and consequently, the relaxation time. This trend is found to be similar to that found earlier in the case of an epoxide/ethylenediamine.[3]

The permittivity ε' and the dielectric loss ε'' were measured for the aged samples and the data obtained are illustrated graphically in Figures 2 and 4. From both figures, it is seen that (1) the values of ε' and ε'' for EPDM samples and those

containing the full ingredients in addition to 35 phr SRF are found to be identical as those before aging; (2) for the samples containing zinc chloride, the values of ε' and ε'' are found to be slightly higher than those for the unaged ones; and (3) for the samples containing ammonium iodide, the values of ε' are found to be slightly less than those before aging, whereas a slight increase in ε'' is noticed.

The obtained data of ε'' for the whole investigated samples were analyzed in the same way as before, and the results obtained are given in Tables V and VI. From both tables, it is interesting to find that at lower concentrations up to 8 phr zinc chloride and 2 phr ammonium iodide, a complete degradation of crosslinking is expected to take place as the values of τ_2 and τ_3 coincide with those obtained before adding such coagents. After these concentrations, a significant increase in τ_2 and τ_3 is noticed but is still lower than those obtained before aging, indicating that a partial degradation of crosslinking is still considered.

The degradation is also detected from the relative contribution of both mechanisms as ε''^* for each process becomes similar to those obtained before crosslinking. This similarity remained almost unchanged up to a concentration of 8 phr zinc chloride and 2 phr ammonium iodide, behind which the contribution is changed. This result supports the increase in τ_2 and τ_3, which is noticed after those concentrations, such as the degradation of crosslinking, have not completely taken place.

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